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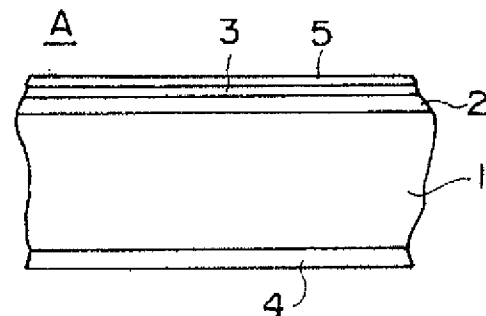
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(54) 【発明の名称】 記録媒体及びその製造方法

(57) 【要約】

【目的】 保護機能に優れ、しかも薄くても充分にその機能が発揮され、かつ、耐久性に富む保護層が設けられた記録媒体を提供することである。

【構成】 支持体と、記録層と、Cを主成分とする保護層とを具備する記録媒体であって、前記保護層にSが含まれている記録媒体。



## 【特許請求の範囲】

【請求項1】 支持体と、記録層と、Cを主成分とする保護層とを具備する記録媒体であって、前記保護層にSが含まれていることを特徴とする記録媒体。

【請求項2】 Cを主成分とする保護層がダイヤモンドライクカーボンであることを特徴とする請求項1の記録媒体。

【請求項3】 保護層中におけるS含有量が0.01～30原子%であることを特徴とする請求項1または請求項2の記録媒体。

【請求項4】 支持体の上に記録層を設ける工程と、前記記録層上にCを主成分とし、Sを含有する保護層を設ける工程とを具備することを特徴とする記録媒体の製造方法。

【請求項5】 保護層を設ける工程が、炭化物および硫化物あるいは炭素・硫黄化合物を反応ガス原料として用いたケミカルベーパーデポジション法によることを特徴とする請求項4の記録媒体の製造方法。

【請求項6】 保護層を設ける工程が、炭化物および硫化物あるいは炭素・硫黄化合物を用いたフィジカルベーパーデポジション法によることを特徴とする請求項4の記録媒体の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、磁気記録媒体などの記録媒体、特にS成分を含有するダイヤモンドライクカーボンで構成されてなる保護層を有する記録媒体に関する。

## 【0002】

【発明の背景】磁気テープ等の磁気記録媒体においては、高密度記録化の要請から、非磁性支持体上に設けられる磁性膜として、バインダ樹脂を用いた塗布型のものではなく、バインダ樹脂を用いない金属薄膜型のものが提案されている。すなわち、無電解メッキ等の湿式メッキ手段、蒸着、スパッタリングあるいはイオンプレーティング等のフィジカルベーパーデポジション(PVD)法による乾式メッキ手段により磁性層を構成した磁気記録媒体が提案されている。そして、この種の磁気記録媒体は磁性体の充填密度が高いことから、高密度記録に適したものである。

【0003】ところで、この種の金属薄膜型の磁気記録媒体における金属磁性膜は磁気ヘッドとの摺動による耐久性に乏しいことから、表面酸化処理を行い、酸化膜による保護膜を設けることが行われている。しかしながら、表面酸化の手段では耐久性の向上効果が少なく、更なる研究が行われている。

【0004】このような観点から、表面酸化膜ではなく、カーボン、特にダイヤモンドライクカーボン等の保護膜を設けることが提案されている。例えば、ケミカルベーパーデポジション(CVD)装置に炭素源としての

C、H<sub>2</sub>ガスを供給し、これからのプラズマガスを金属磁性膜表面に堆積させることにより、表面にダイヤモンドライクカーボンからなる保護膜が設けられた磁気記録媒体が提案(特開平6-41758号公報)されている。

【0005】しかしながら、この提案のものでも充分ではなかった。例えば、剥離が起き、耐久性に問題が残されている。

## 【0006】

10 【発明の開示】本発明の目的は、保護機能に優れ、しかも薄くても充分にその機能が發揮され、かつ、耐久性に富む保護層が設けられた記録媒体を提供することである。この本発明の目的は、支持体と、記録層と、Cを主成分とする保護層とを具備する記録媒体であって、前記保護層にSが含まれていることを特徴とする記録媒体によって達成される。

【0007】又、支持体の上に記録層を設ける工程と、前記記録層上にCを主成分とし、Sを含有する保護層を設ける工程とを具備することを特徴とする記録媒体の製造方法によって達成される。尚、Cを主成分とし、Sを含有する保護層は、炭化物(炭素化合物を含む)および硫化物(硫黄化合物を含む)あるいは炭素・硫黄化合物を反応ガス原料として用いた熱CVD法、熱フィラメントCVD法、光CVD法、プラズマCVD法のようなケミカルベーパーデポジション(CVD)法により作製できる。例えば、メタンやエタン等の鎖状炭化水素、ベンゼンやシクロヘキサン等の環状炭化水素、ピラジン、ピラゾリン、ピラゾール、ピリジン、ピリダジン、ピリミジン、ピペリジン、ピペラジン、イミダゾール、ピロール等の窒素含有環状炭化水素と、水素や酸素などのエッチングガスを併用した反応系に、更に硫化水素や二酸化硫黄などの硫黄(S)含有の反応ガスとをプラズマCVD装置の反応管に供給し、プラズマ化することによりCを主成分とし、Sを含有する保護層が作製できる。あるいは、炭化物(炭素化合物を含む)および硫化物(硫黄化合物を含む)あるいは炭素・硫黄化合物をターゲットとしたスパッタ法や蒸発源とした蒸着法などのフィジカルベーパーデポジション(PVD)法により作製することが出来る。例えば、ガラス状カーボンからなるターゲットに硫黄を置き、これを用いたスパッタによりCを主成分とし、Sを含有する保護層が作製できる。いずれにしても、Cを主成分とし、Sを含有する保護層は、従来から知られている薄膜形成手段を応用することによって作製できる。

【0008】そして、保護層中におけるS含有量は0.01～30原子%、望ましくは0.05～20原子%、より望ましくは0.1～10原子%、更に望ましくは1～5原子%である。すなわち、S含有量が0.01原子%未満の少なすぎると、これを含有させた意味が低下、つまり保護層の耐久性向上効果が小さかったからによ

る。これに対して、S含有量が30原子%を超えて多くなり過ぎた場合には、カーボン層の構造に欠陥が増加し、保護層の強度が低下し、好ましくない傾向があったからによる。

【0009】本発明において、Cを主成分とする保護層は、ダイヤモンド膜、ダイヤモンドライクカーボン膜、アモルファスカーボン膜、グラファイト膜などのような種々のカーボン膜が挙げられるが、硬度が高いダイヤモンド膜やダイヤモンドライクカーボン膜が好ましい。そして、成膜コストや成膜方法のことを考慮すると、ダイヤモンドライクカーボン膜が最も好ましい。すなわち、PVDやCVD手段によりダイヤモンドライクカーボン膜が簡単に成膜できるからである。そして、このような手段によれば、 $-C-S-C-$ 結合を部分的に有するダイヤモンドライクカーボン膜が簡単に得られる。

【0010】この本発明になるCを主成分とし、Sを含有する保護層、特にSを含有するダイヤモンドライクカーボン膜は、20~500Å厚さであることが好ましい。尚、厚さの下限値は30Åであることがより好ましく、そして更に好ましくは40Å、もっと好ましくは50Åである。厚さの上限値は300Åであることがより好ましく、そして更に好ましくは200Å、さらに好ましくは150Å、もっと好ましくは100Å、最も好ましくは90Åである。

【0011】本発明で用いられる磁気記録媒体の支持体は非磁性のものが好ましく、この支持体はPET等のポリエステル、ポリアミド、ポリイミド、ポリスルホン、ポリカーボネート、ポリプロピレン等のオレフィン系の樹脂、セルロース系の樹脂、塩化ビニル系の樹脂などの高分子材料、ガラスやセラミック等の無機系材料などが用いられる。

【0012】この支持体上に蒸着やスパッタ等の乾式メッキ手段によって金属薄膜型の磁性膜（磁性層）が設けられる。尚、蒸着装置やスパッタ装置などは従来から知られているものを用いて差し支えない。金属磁性膜を構成する磁性粒子の材料としては、例えばFe、Co、Ni等の金属の他に、Co-Ni合金、Co-Pt合金、Co-Ni-Pt合金、Fe-Co合金、Fe-Ni合金、Fe-Co-Ni合金、Fe-Co-B合金、Co-Ni-Fe-B合金、Co-Cr合金、あるいはこれらにAl等の金属を含有させたもの等が用いられる。尚、金属磁性膜の成膜時には酸化性ガスなどが供されていて、磁気特性の向上が図られる。

【0013】又、必要に応じて、支持体の他面側にバックコート層が設けられる。このバックコート層は蒸着のような乾式メッキ手段によって構成された非磁性の金属系薄膜であっても、カーボンブラックやバインダ樹脂を含む塗料を塗布することによって構成された塗布型のものであっても良い。磁性膜上には本発明になる保護膜（保護層）が形成される。

【0014】例えば、図2に示す如く、金属磁性膜が支持体上に設けられた磁気記録媒体Aの原反11を真空容器12内に配設された供給側ロール13aから冷却キャンローラ14を経て巻取側ロール13bに走行させ、そしてCVD装置15を作動させ、冷却キャンローラ14に添接されている磁気記録媒体原反の金属磁性膜に対して炭化水素ガスと硫化水素ガスのプラズマを吹き付けると、金属磁性膜の表面にSを含有するダイヤモンドライクカーボン膜が形成される。尚、図2中、16aはH<sub>2</sub>Sガスボンベ、16bはCH<sub>4</sub>ガスボンベ、16cはH<sub>2</sub>ガスボンベ、17はマスフローコントローラ（MFC）、18はスタティックミキサー、19は2.45GHzのマイクロ波発振器、20はプラズマ反応管、21はアイソレータ、22はパワーモニター、23はスリースタブチューナー、24はコイルである。

【0015】以下、具体的な実施例を挙げて本発明を説明する。

#### 【0016】

##### 【実施例】

【実施例1】図1は、本発明になる磁気記録媒体の概略図である。図1中、Aは磁気記録媒体、1は支持体、2は磁性膜、3は保護膜、4はバックコート膜である。

【0017】この磁気記録媒体Aは、先ず、斜め蒸着手段により厚さ2~50μm、例えば6μmで、中心線平均粗さRa1nmのPETフィルム等の非磁性の支持体1の一面上に厚さ2000ÅのCo-Ni（80%~20%）合金磁性膜2を設ける。尚、この磁性膜は、面内保磁力1600Oe、面内飽和磁化6000Gauss、角型比0.9であった。

【0018】又、蒸着手段により、支持体1の他面上に厚さ3000ÅのAl膜（バックコート膜）4を設ける。尚、このバックコート膜4の摩擦係数は0.15であった。上記磁気記録媒体原反11の合金磁性膜上に、図2に示したECRマイクロ波プラズマCVD装置を用いてダイヤモンドライクカーボン膜を66Å厚さ堆積させた。

【0019】尚、このCVD時に導入したガスは、CH<sub>4</sub>が20sccm、H<sub>2</sub>が25sccm、H<sub>2</sub>Sが0.2sccmであり、CH<sub>4</sub>とH<sub>2</sub>Sとの混合ガスを冷却キャンローラ14側口からプラズマ反応管20内に、H<sub>2</sub>を発振器側口からプラズマ反応管20内に導入した。又、供給側ロール13aから-10℃に冷却されている冷却キャンローラ14を経て巻取側ロール13bに走行させた磁気記録媒体原反11の走行速度は0.5m/minであり、真空容器12内の真空度は4×10<sup>-4</sup>Torrである。マイクロ波出力は入射波300W、反射波はスリースタブチューナー23を制御することで30Wとなるようにした。

【0020】上記のようにして得られた保護膜3をXPSスペクトルにより調べた処、Sを1原子%含むダイヤ

モンドライクカーボン膜であった。その後、ダイヤモンドライクカーボン膜上にフッ素系の潤滑剤（モンテカチーニ社のFOMBLIN AM2001）を真空中で超音波噴霧し、20Å厚さの潤滑膜5を付けた。

【0021】そして、8mm幅にスリットし、8mmVTR用カセットに装填した。

【実施例2】実施例1において同様にを行い、厚さ66Åで、Sを5原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【実施例3】実施例1において同様にを行い、厚さ66Åで、Sを0.1原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【0022】【実施例4】実施例1において同様にを行い、厚さ66Åで、Sを10原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【実施例5】実施例1において同様にを行い、厚さ66Åで、Sを0.01原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【0023】【実施例6】実施例1において同様にを行い、厚さ40Åで、Sを5原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【実施例7】実施例1において同様にを行い、厚さ40Åで、Sを0.1原子%含むダイヤモンドライクカーボン\*

\*膜を磁性膜上に設けた。

【0024】【実施例8】実施例1において同様にを行い、厚さ40Åで、Sを10原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【実施例9】実施例1において同様にを行い、厚さ40Åで、Sを0.01原子%含むダイヤモンドライクカーボン膜を磁性膜上に設けた。

【0025】【比較例1】実施例1においてH<sub>2</sub>Sを流さなかった他は同様にを行い、厚さ66Åのダイヤモンドライクカーボン膜を磁性膜上に設けた。

【比較例2】実施例1においてH<sub>2</sub>Sを流さなかった他は同様にを行い、厚さ100Åのダイヤモンドライクカーボン膜を磁性膜上に設けた。

【0026】【特性】上記の各例で得られた8mmVTR用カセットを再生装置（ソニー社のEV-S900改造機）に装填し、23℃、70%RHの雰囲気下、周波数50μHz、パルス率50%、荷重10g、走行速度14mm/sec、ヘッドとの相対速度3.8m/secの条件下においてスチル耐久性を調べたので、その結果を表-1に示す。又、スチル耐久性試験に用いた8mmVTRを用いて再生出力も調べたので、併せて表-1に示す。

【0027】

	スチル耐久性 (分)	再生出力 (dB)
実施例1	>120	0.1
実施例2	>120	-0.2
実施例3	>120	0.2
実施例4	>120	0.1
実施例5	>120	-0.1
実施例6	>120	0.5
実施例7	>120	0.6
実施例8	>120	0.6
実施例9	>120	0.5
比較例1	60	0.0
比較例2	>120	-1.1

\*スチル耐久性は出力が初期値より6dB低下するまでの時間

\*再生出力は比較例1を基準

これによれば、磁性膜表面に設けたダイヤモンドライクカーボン膜にSを含有してなるものは、耐久性に富むことが判る。特に、その厚さが40Åと言ったような薄いものでも耐久性に富むものであり、これよりスペーシングロスを少なく出来るから、それだけ再生出力も大きなものとなる。

【0028】

【効果】本発明によれば、耐久性および再生出力に優れた記録媒体が得られる。

【図面の簡単な説明】

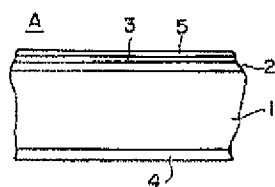
【図1】磁気記録媒体の概略図

【図2】ダイヤモンドライクカーボン成膜装置の概略図

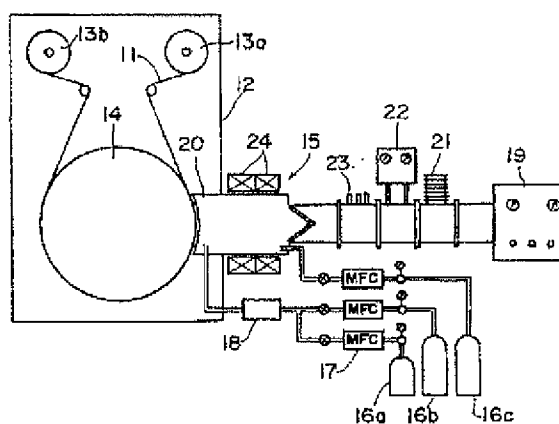
【符号の説明】

- A 磁気記録媒体
- 1 支持体
- 2 磁性膜
- 3 保護膜
- 4 バックコート膜
- 5 潤滑膜

【図1】



【図2】



フロントページの続き

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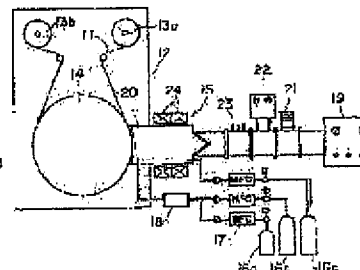
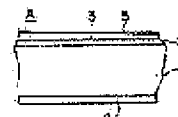
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KITAORI NORIYUKI  
YOSHIDA OSAMU  
MIZUNOYA HIROHIDE  
SHIGA AKIRA

## (54) RECORDING MEDIUM AND PRODUCTION THEREOF

## (57)Abstract:

PURPOSE: To obtain a recording medium excellent in durability and reproducing output by constituting the medium of a supporting body, recording layer, and protective layer essentially comprising C and incorporating S into the protective layer.

CONSTITUTION: The raw web 11 of a magnetic recording medium A having a metal magnetic film on a supporting body is travelled from a supply roll 13a to a winding roll 13b along a cooling can roller 14 in a vacuum chamber 12. A CVD device 15 is operated to spray the plasma of hydrocarbon gas and hydrogen sulfide gas to the metal magnetic film of the magnetic recording medium web travelling along the cooling can roller 14. Thus, a diamond like carbon film containing S is formed on the surface of the metal magnetic film.

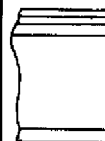


JAPANESE [JP,08-102052,A]

Drawing  
selection

Repre

A



[Translation  
done.]

1. JP,08-102052,A(1996)

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION EXAMPLE DESCRIPTION OF  
DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]A base material.

A recording layer.

A protective layer which uses C as the main ingredients.

It is the recording medium provided with the above, and S is contained in said protective layer.

[Claim 2]A recording medium of claim 1, wherein a protective layer which uses C as the main ingredients is diamond like carbon.

[Claim 3]A recording medium of claim 1, wherein S content in a protective layer is 0.01-30atom%, or claim 2.

[Claim 4]A manufacturing method of a recording medium characterized by comprising the following.

A process of providing a recording layer on a base material.

A process of providing a protective layer which uses C as the main ingredients on said recording layer, and contains S.

[Claim 5]A manufacturing method of a recording medium of claim 4, wherein a process of providing a protective layer is based on the chemical vapor deposition method using carbide and a sulfide, or carbon and a sulfur compound as a reactant gas raw material.

[Claim 6]A manufacturing method of a recording medium of claim 4, wherein a process of providing a protective layer is based on the physical vapor deposition method using carbide and a sulfide, or carbon and a sulfur compound.

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BACK

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DETAILED DESCRIPTION [Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to recording media, such as a magnetic recording medium, and the recording medium which has a protective layer which it comes to comprise diamond like carbon containing especially S ingredient.

[0002]

[Background of the Invention]In magnetic recording media, such as magnetic tape, not the thing of the coating mold using binder resin as a magnetic film provided on a nonmagnetic substrate but the metal thin film type thing which does not use binder resin is proposed from the request of high-density-recording-izing. That is, the magnetic recording medium which constituted the magnetic layer by the dry type plating means by the physical vapor deposition (PVD) methods, such as wet plating means, such as electroless deposition, vacuum evaporation, sputtering, or ion plating, is proposed. And since the pack density of a magnetic body is high, this kind of magnetic recording medium fits high density recording.

[0003]By the way, since the metallic magnetic film in a this kind of metal thin film type magnetic recording medium is lacking in the endurance by sliding with a magnetic head, scaling processing is performed and providing the protective film by an oxide film is performed. However, by the means of scaling, there are few durable improved effects and further research is done.

[0004]From such a viewpoint, providing protective films, such as not a surface oxide film but carbon, especially diamond like carbon, is proposed. For example, by supplying the C<sub>6</sub>H<sub>6</sub> gas as a carbon source to a chemical vapor deposition (CVD) device, and making future plasma gas deposit on the metallic magnetic film surface, The magnetic recording medium with which the protective film which consists of diamond like carbon was provided in the surface is proposed (JP,6-41758,A).

[0005]However, the thing of this proposal was not enough, either. For example, exfoliation breaks out and the problem is left behind to endurance.

[0006]



[Description of the Invention]The purpose of this invention is to provide the recording medium with which the protective layer which it excels in a protection feature, the function is moreover fully exhibited even if thin, and is rich in endurance was provided. The purpose of this this invention is a recording medium possessing a base material, a recording layer, and the protective layer that uses C as the main ingredients, and is attained by the recording medium, wherein S is contained in said protective layer.

[0007]It is attained by the manufacturing method of the recording medium possessing the process of providing a recording layer on a base material, and the process of providing the protective layer which uses C as the main ingredients on said recording layer, and contains S. The protective layer which uses C as the main ingredients and contains S, It is producible by a heat CVD method, a hot filament CVD method, an optical CVD method, and a chemical vapor deposition (CVD) method like plasma CVD method using carbide (carbon compounds are included) and the sulfide (a sulfur compound is included), or carbon and a sulfur compound as a reactant gas raw material. For example, cyclic hydrocarbon, such as chain hydrocarbon, such as methane and ethane, benzene, and cyclohexane, Nitrogen content cyclic hydrocarbon, such as pyrazine, pyrazolidine, pyrazoline, a pyrazole, pyridine, pyridazine, pyrimidine, piperidine, a piperazine, imidazole, and pyrrole, By supplying the reactant gas of sulfur (S) content, such as hydrogen sulfide and sulfur dioxide, to the coil of a plasma CVD device, and plasma-izing it further, to the system of reaction which used etching gas, such as hydrogen and oxygen, together, C is used as the main ingredients and the protective layer containing S can be produced. Or it is producible by the physical vapor deposition (PVD) methods, such as vacuum deposition made into the sputtering technique which targeted carbide (carbon compounds are included) and the sulfide (a sulfur compound is included), or carbon and a sulfur compound, or the evaporation source. For example, sulfur is put on the target which consists of glassy carbon, C is used as the main ingredients by the weld slag using this, and the protective layer containing S can be produced. Anyway, the protective layer which uses C as the main ingredients and contains S is producible by applying a thin-film-forming means by which it is known from the former.

[0008]and S content in a protective layer -- 0.01-30atom% -- desirable -- 0.05-20atom% -- more -- desirable -- 0.1-10atom% -- it is 1 - pentatomic % still more desirably. That is, since the fall of the meaning [ that there is little S content ] of less than 0.01 atom % which made this contain when it elapsed, i.e., the endurance improved effect of a protective layer, was small, it depends. On the other hand, when S content increases too much exceeding 30 atom %, a defect increases to the structure of a carbon layer and the intensity of a protective layer falls, and since there was a tendency which is not preferred, it depends.

[0009]In this invention, the protective layer which uses C as the main ingredients has preferred diamond membrane and diamond like carbon film with high hardness, although various carbon films, such as diamond membrane, a diamond like carbon film, an amorphous carbon film, and a graphite film, are mentioned. And when the thing of membrane formation cost or a method for film deposition is taken into consideration, a diamond like carbon film is the most preferred. That is, it is because a diamond like carbon film can form membranes easily by PVD or a CVD means. And according to such a means, the diamond like carbon film which has -C-S-C-combination selectively is obtained simply.

[0010]As for the protective layer which uses as the main ingredients C which becomes this this invention, and contains S, and the diamond like carbon film containing especially S, it is preferred that it is 20-500A thickness. 40 A of lower limits of thickness are 50A more preferably still more preferably [ it is more preferred that it is 30A, and ]. 200 A of upper limit [ 150 A of / 100 A of ] of thickness is 90A most preferably still more preferably still more preferably [ it is more preferred that it is 300A, and ].

[0011]The nonmagnetic thing of the base material of the magnetic recording medium used by this invention is preferred, As for this base material, inorganic system materials of polyester, such as PET, polyamide, polyimide, polysulfone, polycarbonate, polypropylene, etc., such as polymer materials, such as resin of an olefin system, resin of a cellulose type, and resin of a VCM/PVC system, glass, and ceramics, etc. are used.

[0012]A metal thin film type magnetic film (magnetic layer) is provided by dry type plating means, such as vacuum evaporation and weld slag, on this base material. Neither an evaporation apparatus nor a sputter device interferes using what is known from the former. As a material of the magnetic particle which constitutes a metallic magnetic film, Besides metal, such as Fe, Co, and nickel, for example, Co-Ni alloy, Co-Pt alloy, A Co-nickel-Pt alloy, Fe-Co alloy, a Fe-Ni alloy, a Fe-Co-Ni alloy, a Fe-Co-B alloy, a Co-nickel-Fe-B alloy, Co-Cr alloy, or the thing that made these contain metal, such as aluminum, is used. The oxidizing gas etc. are offered at the time of membrane formation of a metallic magnetic film, and improvement in magnetic properties is achieved.

[0013]moreover -- accepting necessity -- a base material -- on the other hand, a back coat layer is provided in a side. Even if this back coat layer is the nonmagnetic metal system thin film constituted by a dry type plating means like vacuum evaporation, it may be a thing of the coating mold constituted by applying the paint containing carbon black and binder resin. On a magnetic film, the protective film (protective layer) which becomes this invention is formed.

[0014]For example, as shown in drawing 2, a metallic magnetic film runs the rolling-up side roll 13b the original fabric 11 of the magnetic recording medium A formed on the base material through the cooling can

roller 14 from the supply side roll 13a allocated in the vacuum housing 12, And CVD system 15 is operated, and if the plasma of hydrocarbon gas and gaseous hydrogen sulfide is sprayed to the metallic magnetic film of the magnetic-recording-medium original fabric by which the splice is carried out to the cooling can roller 14, the diamond like carbon film which contains S on the surface of a metallic magnetic film will be formed. An H<sub>2</sub>S gas bomb and 16b 16a among drawing 2 CH<sub>4</sub> gas bomb, H<sub>2</sub> gas bomb and 17 16c A massflow controller (MFC), 18 -- as for an isolator and 22, a 2.45-GHz microwave oscillator and 20 are [ a three stub tuner and 24 ] coils a power monitor and 23 a plasma reaction pipe and 21 a static mixer and 19.

[0015]Hereafter, a concrete example is given and this invention is explained.

[0016]

[Example]

[Example 1] Drawing 1 is a schematic diagram of the magnetic recording medium which becomes this invention. A of a base material and 2 is [ a protective film and 4 ] back coat films a magnetic film and 3 a magnetic recording medium and 1 among drawing 1.

[0017]First, by a slanting vacuum evaporation means, this magnetic recording medium A is 2-50 micrometers in thickness, for example, 6 micrometers, and forms the 2000-Å-thick Co-nickel (80%-20%) alloy magnetic film 2 on the whole surface of the nonmagnetic base material 1 of the PET film of arithmetical-mean-deviation-of-profile Ra1nm, etc. This magnetic film was coercive force 1600Oe within a field, saturation magnetization 6000Gauss within a field, and the square-shaped ratio 0.9.

[0018]a vacuum evaporation means -- the base material 1 -- on the other hand, 3000-Å-thick Al film (back coat film) 4 is formed upwards. The coefficient of friction of this back coat film 4 was 0.15. On the alloy magnetic film of the above-mentioned magnetic-recording-medium original fabric 11, the 66Å thickness deposition of the diamond like carbon film was carried out using the ECR microwave plasma CVD system shown in drawing 2.

[0019]In CH<sub>4</sub>, 20sccm and H<sub>2</sub> is [ 25sccm and H<sub>2</sub>S of the gas introduced at the time of this CVD ] 0.2sccm.

The mixed gas of CH<sub>4</sub> and H<sub>2</sub>S was introduced in the plasma reaction pipe 20 from cooling can roller 14 side vent, and H<sub>2</sub> was introduced in the plasma reaction pipe 20 from the oscillator side vent.

The travel speeds of the magnetic-recording-medium original fabric 11 the rolling-up side roll 13b was run through the cooling can roller 14 cooled by -10 °C from the supply side roll 13a are 0.5 m/min, and the degree of vacuum in the vacuum housing 12 is  $4 \times 10^{-3}$  Torr. It was made to be set to 30W because a microwave output controls the incident wave 300W and a reflected wave controls the three stub tuner 23.

[0020]one atom % It was an included diamond like carbon film about the place and S which investigated the protective film 3 produced by performing it above by the XPS spectrum. Then, on the diamond like carbon film, ultrasonic atomization of the lubricant (FOMBLIN AM2001 of Montecatini) of a fluorine system was carried out in the vacuum, and the lubricating film 5 of 20A thickness was attached.

[0021]And the slit was carried out to 8-mm width, and the cassette for 8mmVTR was loaded.

[Example 2] In Example 1, it carried out similarly and the diamond like carbon film which pentatomic % Contains S at 66 A in thickness was provided on the magnetic film.

[Example 3] In Example 1, it carried out similarly and the diamond like carbon film which 0.1 atom % Contains S at 66 A in thickness was provided on the magnetic film.

[0022][Example 4] In Example 1, it carried out similarly and the diamond like carbon film which ten atom % Contains S at 66 A in thickness was provided on the magnetic film.

[Example 5] In Example 1, it carried out similarly and the diamond like carbon film which 0.01 atom % Contains S at 66 A in thickness was provided on the magnetic film.

[0023][Example 6] In Example 1, it carried out similarly and the diamond like carbon film which pentatomic % Contains S at 40 A in thickness was provided on the magnetic film.

[Example 7] In Example 1, it carried out similarly and the diamond like carbon film which 0.1 atom % Contains S at 40 A in thickness was provided on the magnetic film.

[0024][Example 8] In Example 1, it carried out similarly and the diamond like carbon film which ten atom % Contains S at 40 A in thickness was provided on the magnetic film.

[Example 9] In Example 1, it carried out similarly and the diamond like carbon film which 0.01 atom % Contains S at 40 A in thickness was provided on the magnetic film.

[0025][Comparative example 1] H<sub>2</sub>S was not passed in Example 1, and also it carried out similarly, and the 66-A-thick diamond like carbon film was provided on the magnetic film.

[Comparative example 2] H<sub>2</sub>S was not passed in Example 1, and also it carried out similarly, and the 100-A-thick diamond like carbon film was provided on the magnetic film.

[0026][Characteristic] Playback equipment (EV-S900 modified machine of Sony Corp.) is loaded with the cassette for 8mmVTR obtained in each of above-mentioned examples, Under the atmosphere of 23 \*\* and 70%RH, since still durability was investigated under the with frequency 50microHz, 50% of a pulse ratio, 10 g of load, the travel speed of 14 mm/sec, and a relative velocity [ with a head ] of 3.8 m/sec condition, the result is shown in table-1. Since the reproducing output was also

investigated using 8mmVTR used for the still durability examination, it is collectively shown in table-1.

[0027]

Table-1 Still durability (minute) Reproducing output (dB)

Example 1 > 120 0.1 Example 2 > 120. -0.2 example 3 > 120 0.2

Example 4. >120 0.1 example 5 > 120 -0.1 Example 6. >120 0.5

example 7 > 120 0.6 example 8 > 120 0.6 example 9 > 120 0.5

comparative example 1 60 0.0 comparative example 2 > 120 Time until the output of -1.1 \* still durability declines by 6 dB from an initial value \* reproducing output the comparative example 1. a standard -- according to this, it turns out that what contains S in the diamond like carbon film provided in the magnetic film surface is rich in endurance. Since a thin thing which the thickness said as 40 Å especially is also rich in endurance and can make spacing loss less than this, it becomes what also has a so big reproducing output.

[0028]

[Effect]According to this invention, the recording medium excellent in endurance and a reproducing output is obtained.

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TECHNICAL FIELD [Industrial Application]This invention relates to recording media, such as a magnetic recording medium, and the recording medium which has a protective layer which it comes to comprise diamond like carbon containing especially S ingredient.  
[0002]

[Background of the Invention]In magnetic recording media, such as magnetic tape, not the thing of the coating mold using binder resin as a magnetic film provided on a nonmagnetic substrate but the metal thin film type thing which does not use binder resin is proposed from the request of high-density-recording-izing. That is, the magnetic recording medium which constituted the magnetic layer by the dry type plating means by the physical vapor deposition (PVD) methods, such as wet plating means, such as electroless deposition, vacuum evaporation, sputtering, or ion plating, is proposed. And since the pack density of a magnetic body is high, this kind of magnetic recording medium fits high density recording.

[0003]By the way, since the metallic magnetic film in a this kind of metal thin film type magnetic recording medium is lacking in the endurance by sliding with a magnetic head, scaling processing is performed and providing the protective film by an oxide film is performed. However, by the means of scaling, there are few durable improved effects and further research is done.

[0004]From such a viewpoint, providing protective films, such as not a surface oxide film but carbon, especially diamond like carbon, is proposed. For example, by supplying the C<sub>6</sub>H<sub>6</sub> gas as a carbon source to a chemical vapor deposition (CVD) device, and making future plasma gas deposit on the metallic magnetic film surface, The magnetic recording medium with which the protective film which consists of diamond like carbon was provided in the surface is proposed (JP,6-41758,A).

[0005]However, the thing of this proposal was not enough, either. For example, exfoliation breaks out and the problem is left behind to endurance.

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[Description of the Invention]The purpose of this invention is to provide the recording medium with which the protective layer which it excels in a

protection feature, the function is moreover fully exhibited even if thin, and is rich in endurance was provided. The purpose of this invention is a recording medium possessing a base material, a recording layer, and the protective layer that uses C as the main ingredients, and is attained by the recording medium, wherein S is contained in said protective layer. [0007]It is attained by the manufacturing method of the recording medium possessing the process of providing a recording layer on a base material, and the process of providing the protective layer which uses C as the main ingredients on said recording layer, and contains S. The protective layer which uses C as the main ingredients and contains S, It is producible by a heat CVD method, a hot filament CVD method, an optical CVD method, and a chemical vapor deposition (CVD) method like plasma CVD method using carbide (carbon compounds are included) and the sulfide (a sulfur compound is included), or carbon and a sulfur compound as a reactant gas raw material. For example, cyclic hydrocarbon, such as chain hydrocarbon, such as methane and ethane, benzene, and cyclohexane, Nitrogen content cyclic hydrocarbon, such as pyrazine, pyrazolidine, pyrazoline, a pyrazole, pyridine, pyridazine, pyrimidine, piperidine, a piperazine, imidazole, and pyrrole, By supplying the reactant gas of sulfur (S) content, such as hydrogen sulfide and sulfur dioxide, to the coil of a plasma CVD device, and plasma-izing it further, to the system of reaction which used etching gas, such as hydrogen and oxygen, together, C is used as the main ingredients and the protective layer containing S can be produced. Or it is producible by the physical vapor deposition (PVD) methods, such as vacuum deposition made into the sputtering technique which targeted carbide (carbon compounds are included) and the sulfide (a sulfur compound is included), or carbon and a sulfur compound, or the evaporation source. For example, sulfur is put on the target which consists of glassy carbon, C is used as the main ingredients by the weld slag using this, and the protective layer containing S can be produced. Anyway, the protective layer which uses C as the main ingredients and contains S is producible by applying a thin-film-forming means by which it is known from the former.

[0008]and S content in a protective layer -- 0.01-30atom% -- desirable -- 0.05-20atom% -- more -- desirable -- 0.1-10atom% -- it is 1 - pentatomic % still more desirably. That is, since the fall of the meaning [ that there is little S content ] of less than 0.01 atom % which made this contain when it elapsed, i.e., the endurance improved effect of a protective layer, was small, it depends. On the other hand, when S content increases too much exceeding 30 atom %, a defect increases to the structure of a carbon layer and the intensity of a protective layer falls, and since there was a tendency which is not preferred, it depends.

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membrane, a diamond like carbon film, an amorphous carbon film, and a graphite film, are mentioned. And when the thing of membrane formation cost or a method for film deposition is taken into consideration, a diamond like carbon film is the most preferred. That is, it is because a diamond like carbon film can form membranes easily by PVD or a CVD means. And according to such a means, the diamond like carbon film which has -C-S-C-combination selectively is obtained simply.

[0010]As for the protective layer which uses as the main ingredients C which becomes this invention, and contains S, and the diamond like carbon film containing especially S, it is preferred that it is 20-500A thickness. 40 A of lower limits of thickness are 50A more preferably still more preferably [ it is more preferred that it is 30A, and ]. 200 A of upper limit [ 150 A of / 100 A of ] of thickness is 90A most preferably still more preferably still more preferably [ it is more preferred that it is 300A, and ].

[0011]The nonmagnetic thing of the base material of the magnetic recording medium used by this invention is preferred, As for this base material, inorganic system materials of polyester, such as PET, polyamide, polyimide, polysulfone, polycarbonate, polypropylene, etc., such as polymer materials, such as resin of an olefin system, resin of a cellulose type, and resin of a VCM/PVC system, glass, and ceramics, etc. are used.

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[0014]For example, as shown in drawing 2, a metallic magnetic film runs the rolling-up side roll 13b the original fabric 11 of the magnetic recording medium A formed on the base material through the cooling can roller 14 from the supply side roll 13a allocated in the vacuum housing 12, And CVD system 15 is operated, and if the plasma of hydrocarbon gas and gaseous hydrogen sulfide is sprayed to the metallic magnetic



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Table-1 Still durability (minute) Reproducing output (dB)

Example 1 > 120 0.1 Example 2 > 120. -0.2 example 3 > 120 0.2  
Example 4. >120 0.1 example 5 > 120 -0.1 Example 6. >120 0.5  
example 7 > 120 0.6 example 8 > 120 0.6 example 9 > 120 0.5  
comparative example 1 60 0.0 comparative example 2 > 120 Time until  
the output of -1.1 \* still durability declines by 6 dB from an initial value \*  
reproducing output the comparative example 1. a standard -- according  
to this, it turns out that what contains S in the diamond like carbon film  
provided in the magnetic film surface is rich in endurance. Since a thin  
thing which the thickness said as 40 Å especially is also rich in endurance  
and can make spacing loss less than this, it becomes what also has a so  
big reproducing output.

JAPANESE

[JP,08-102052,A]

Drawing  
selection

Repre

A



[Translation  
done.]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION EXAMPLE DESCRIPTION OF  
DRAWINGS DRAWINGS

1. JP,08-102052,A(1996)

[Translation done.]

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- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]The schematic diagram of a magnetic recording medium

[Drawing 2]The schematic diagram of a diamond like carbon film deposition system

[Description of Notations]

A Magnetic recording medium

1 Base material

2 Magnetic film

3 Protective film

4 Back coat film

5 Lubricating film

[Translation done.]

BACK

NEXT



1. JP,08-102052,A(1996)

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DRAWINGS DRAWINGS

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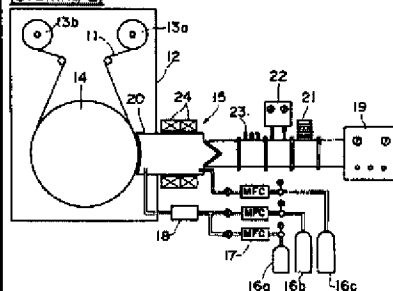
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

BACK

NEXT